Electrical and Optical Study of Dy doped Bismuth Layer $SrBi_2Ta_2O_9$(SBT)

A Dissertation submitted in partial fulfilment

FOR THE DEGREE OF MASTER OF SCIENCE IN PHYSICS

Under Academic Autonomy

NATIONAL INSTITUTE OF TECHNOLOGY, ROURKELA

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CERTIFICATE

This is to certify that the thesis entitled, **"Electrical and Optical Study of Dy doped Bismuth Layer $SrBi_2Ta_2O_9$ (SBT)"** submitted by Rakesh Kumar Sahu in partial fulfillments for the requirements for the award of Master of Science Degree in Physics Department at National Institute of Technology, Rourkela is an authentic work carried out by him under my supervision and guidance.

To the best of my knowledge, the matter embodied in the project has not been submitted to any other University/Institute for the award of any Degree or Diploma.

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Rourkela Rakesh Kumar Sahu

Date:

ABSTRACT:

The two layer Aurivillius compound $SrBi_2Ta_2O_9$ (SBT) and $SrBi_{2-x}Dy_xTa_2O_9$ (x=0.025, 0.05, 0.1) was synthesized by using a solid state sintering method. The X-ray diffraction (XRD) analysis revealed that the dysprosium substituted ceramic $SrBi_2Ta_2O_9$ have a pure two-layer Aurivillius type structure. The effects of Dysprosium oxide on the microstructure, ferroelectric, dielectric and optical properties of the ceramics were investigated. D_y doping is found to be significantly affect on the structural and physical properties of SBT. The dielectric constant (Ɛ) and transition temperature (T_c) of Dy-doped samples was found to be decrease with increase of Dy content. Well-developed P (polarization)-E (Electric field) hysteresis loops were observed for all the samples and also the band-gap (E_g) of this sample was verify by UV-VIS spectrophotometer.

CONTENTS

List of Fig.-

Chapter-1

1 *Introduction:-*

The ferroelectric materials are technologically an important class of material that shows a variety of phenomena. These materials have high permittivity, high piezoelectric and pyroelectric coefficient, electro-optic properties, tunability of permittivity, switching of polarization.

These properties are very useful in the application of IR detector, piezo sensors, actuators, nonvolatile ferroelectric memory, DRAM, Decoupling capacitors, display, shutter, phase shifter, high Q resonators.

1.1 *Piezoelecticity:-*

Some materials possess the ability to produce electricity by applying mechanical stress. This effect is known as piezoelectric effect. The stress can also be developed by hitting or twisting the material by deforming the crystal lattice without fracturing called as direct piezoelectric effect. Piezoelectric materials also show a reverse or converse effect, where the geometric strain (deformation) can produced by the application of a voltage. Both the direct and converse piezoelectric effects are expressed in tensor notation as:-

$P_i = d_{ijk}\alpha_{jk}$(for direct piezoelectric effect)

$\beta_{ij} = d_{ijk}E_k$(for converse piezoelectric effect)

For direct piezoelectric effect

Where P_i = polarization generated along the *i*– axis in response to the applied stress,

d_{ijk}= piezoelectric coefficient.

And for the converse effect

β_{ij}= strain generated in particular orientation of the crystal up on the application of electric field along the *k* – axis.

1.2Pyroelectricity:-

Certain crystals produce electric polarity by a change of temperature. Also certain dielectric (electrically non-conducting) crystals develop an electric polarization (dipole moment per unit volume) up on uniform temperature change. In crystal this piezoelectric effect requires lack a center of symmetry and a polar directions (i.e., a polar axis) along which charge carrier reached the surface. However, when the temperature of the crystal is raised or lowered, the polarization changes. This requirement is fulfilled for 10 out of 32 crystal classes. Some examples of pyroelectric material are lithium sulfate monohydrate, tourmaline, barium titanate, and cane sugar.

Pyroelectrics materials are used in a broad spectrum of scientific and technical applications. The most infrared radiation detectors and sensors contain pyroelectric material. These are also used to measure the power generated by a radiation source i.e. in radiometry, or the temperature of a remote hot body i.e. in pyrometry. Other applications of pyroelectricity are in pyroelectric plate, solar energy conversion, refrigeration, information storage, and solid-state science.

1.3Ferroelectricity:-

Some crystal possesses reversible spontaneous polarization as exhibited by a dielectric hysteresis loop are known as ferroelectric crystal. Uniform polarization region in ferroelectric crystal are called ferroelectric domains where all dipoles are aligned in same direction within the domain. The domains in a crystal are separated by interfaces called domain walls. By applying very strong field one can align domain polarization in single direction, known as domain switching. All ferroelectric materials are pyroelectric in nature, but the reverse is not true. Below a certain temperature called transition temperature or Curie temperature, all ferroelectric and pyroelectric materials are polar and possess a spontaneous polarization (electric dipole moment). Above the Curie temperature the non-polar phase encountered, known as the paraelectric phase. The direction of the spontaneous polarization conforms the crystal symmetry of the material, while the re-orientation of the spontaneous polarization is a result of atomic displacements in crystals. The spontaneous polarization is greatest in magnitude at temperatures well below the Curie temperature.

The ferroelectric crystal shows the hysteresis loop (i.e. is shown in **fig. 1**). As the applied electric field strength is increased, the domains start to align in the positive direction giving rise to a rapid increase in the polarization. At very high field, the polarization reaches a saturation value (Ps). But the polarization does not fall to zero when the external field is removed. At zero external field, still some of the domains remain aligned in the positive direction. This polarization is called remnant polarization (Pr).to make polarization to zero. The external field needed to reduce the Pr is called the coercive field strength (Ec). If the field is further increased to more in negative value, the direction of polarization flips and a hysteresis loop is obtained. The spontaneous polarization **Ps** is obtained by extrapolating the curve onto the polarization axes.

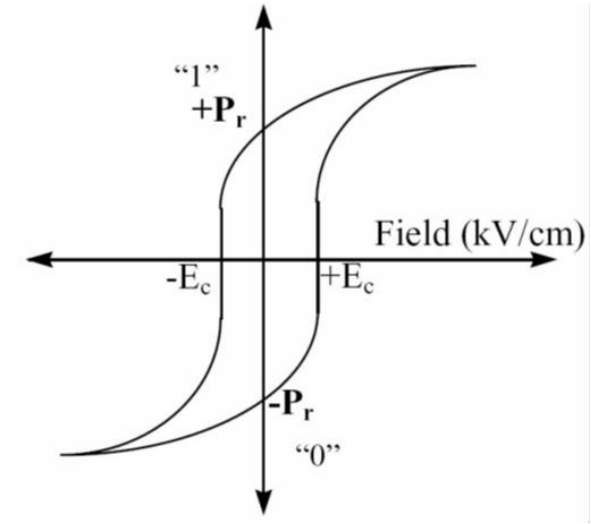

Fig1. P-E Loop or Hysteresis Loop

1.4 Origin of ferroelectric in crystal:-

All Crystal can be divided into 32 possible crystal classes (i.e. point groups), out of which 11 are Centro symmetric and thus they cannot exhibit polar properties. The remaining 21 are lack of Centro symmetry and thus they possess one or more polar axes. Among these, 20 classes are piezoelectric, the one exception being cubic class (Fig 2). Piezoelectric crystals have the property that the application of mechanical stress induces polarization, and conversely, the application of an electric field produces mechanical deformation. Of the 20 piezoelectric classes, 10 have a unique

polar axis and thus are spontaneously polarized, i.e. polarized in the absence of an electric field. Crystals belonging to these 10 classes are called pyroelectric. The intrinsic polarization of pyroelectric crystals is often difficult to detect experimentally because of the neutralization of the charges on the crystal surfaces by free charges from the atmosphere and by conduction within the crystal. However, because the polarization is a function of temperature, it is often possible to observe the spontaneous moment in these crystals by changing the temperature, hence the name Pyroelectrics. Ferroelectric crystals belong to the pyroelectric family, but they also exhibit the additional property that the direction of the spontaneous polarization can be reversed by the application of an electric field.

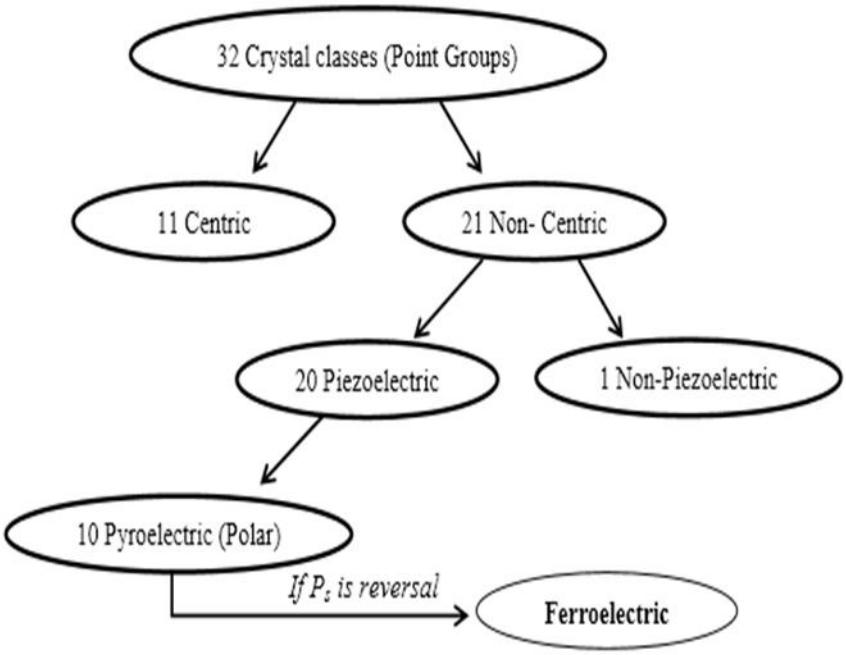

Fig2:-Classification of Crystals Classes

1.5 Dielectrics :-

Dielectrics are material that permits the passage of the electric field. The energy gap of dielectric is higher than that of semiconductors, so thermally generated charge carriers are generally absent. So at room temperature dielectric material behaves as an insulator. But in the presence of electric field charge does not flow through the

dielectric material as in a conductor but only slightly shift from their average equilibrium positions cause polarization. In dielectrics, the charge center shifts according to the fields causes various type of polarization.

Polarization types:-

1-Electronicpolarization

Polarization arises due to the displacement of electrons with respect to the nuclei with which they are associated, by the application of an external electric field.

2- Ionic polarization

In an electric field, the ions in ionic crystals feel forces in opposite directions which give rise to polarization.

3- Orientational / Dipolar polarization,

Materials with built-in dipoles that are independent of each other and rotate freely gives rise to Dipolar Polarization.

4- Space charge polarization.

Accumulation of charge in the grain boundary leads to space charge polarization in the material.

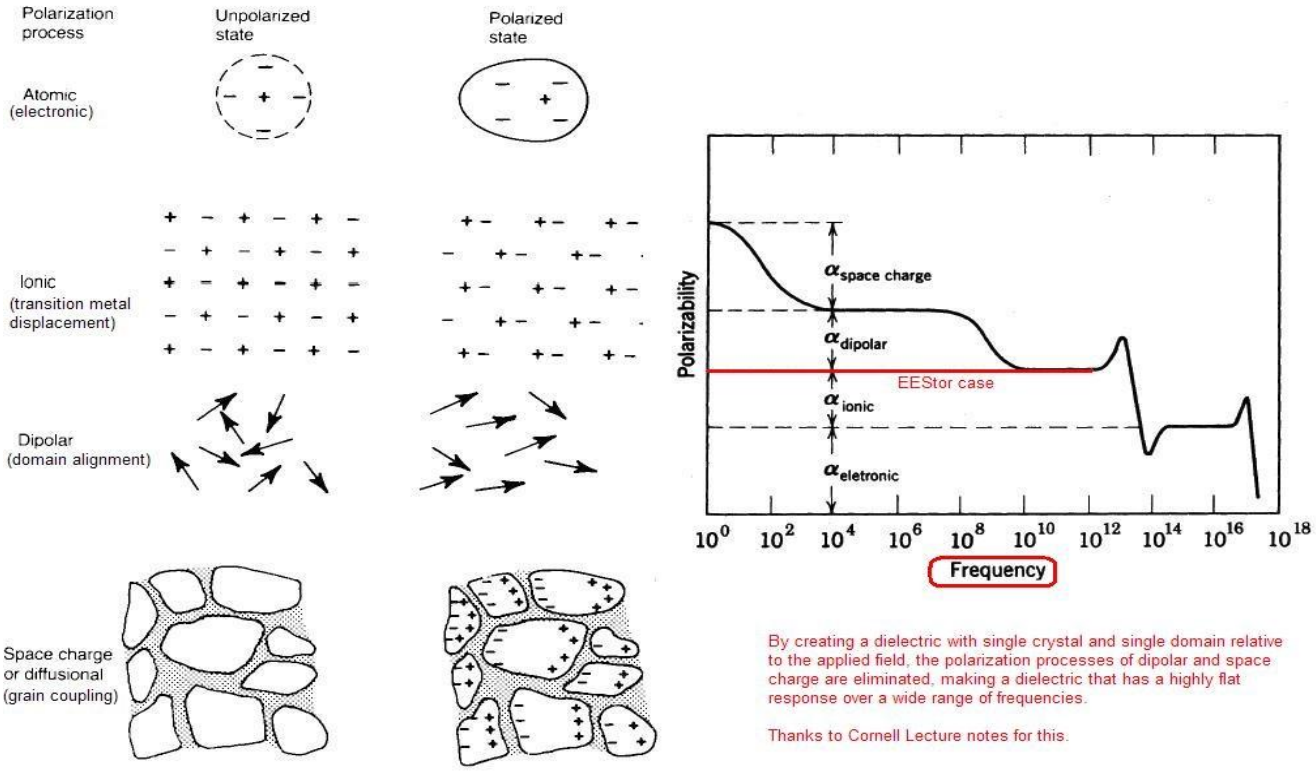

Fig3: Types of Polarization

1.6 Bismuth Layer Ferroelectric Structures:-

Layer perovskite StrontiumBismuthTantalate(SBT)is a member of bismuth layer structure ferroelectric with general formula$[Bi_2O_2]^{2+}[A_{m-1}B_mO_{3m+1}]^{2-}$ .Where $A=Na^+,K^+,Ba^{2+},Ca^{2+},Pb^{2+},Sr^{2+},Bi^{2+}$larger cations, $B=Fe^{3+},Ti^{4+},Nb^{5+},Ta^{5+},W^{6+}$ smaller cat-ion and m indicates the no. of the corner sharing octahedra forming the perovskite like slabs.

The crystal structure SBT comprises of pseudo perovskite blogs $(SrTa_2O_7)^{2-}$ that are sandwich between $(Bi_2O_2)^{2-}$layers.

In $SrBi_2Ta_2O_9$(SBT)Sr^{2+}occupies the A site of the perovskite andTa^{5+}occupies the B site of the perovskite and m is equal to 2.

1.7 Relaxor Ferroelectrics:-

This type of material possesses slim PE loop with diffuse phase transition. The temperature at which the dielectric constant is maximum shifts to higher temperature with increase in frequency. This type of behavior is due to the compositional disorder by the formation of polar micro regions (PMR).PMR sizes vary and it may follow distribution at high temperature.as temperature decreases the average size of PMR increases. The figure below shows the behavior of normal ferroelectric and relaxor ferroelectric.

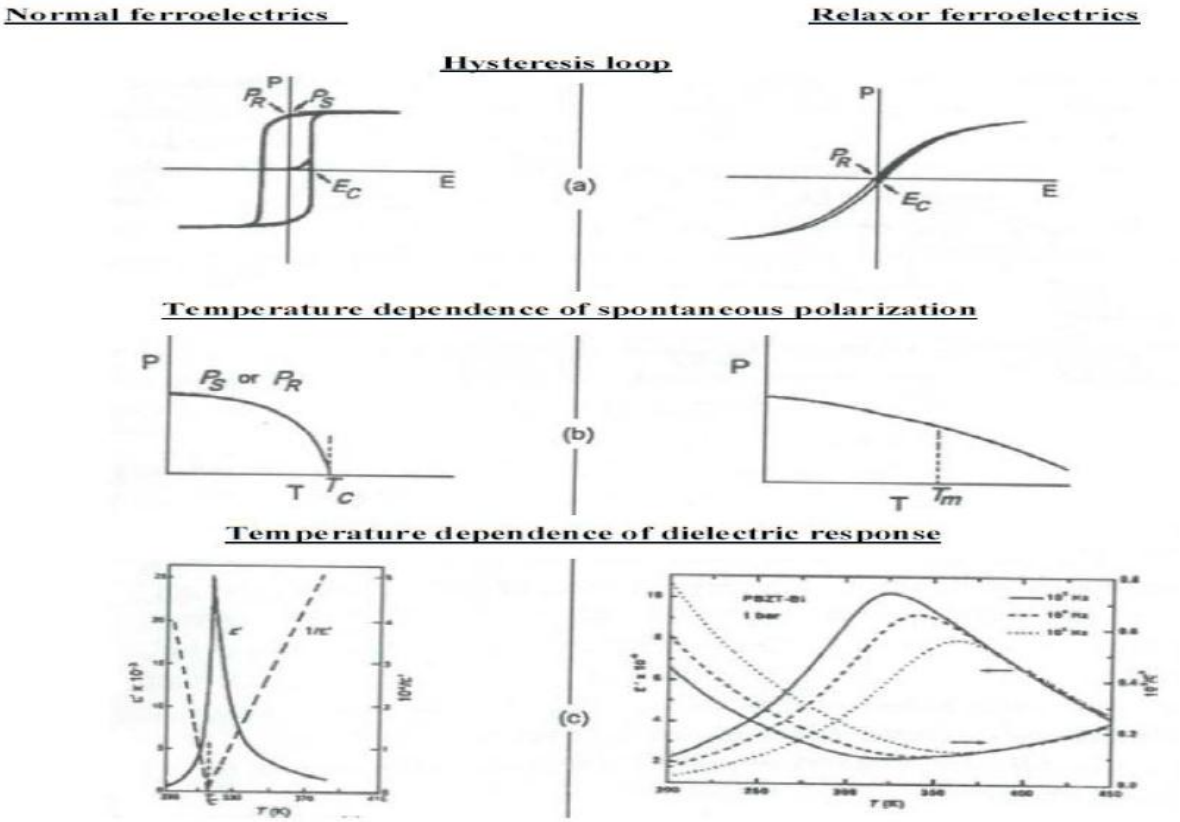

Fig4: Comparisons of Normal to Relaxor ferroelectric

1.8 Literature Survey:-

In the world of ferroelectric material and its applications in various electronics fields such as ferroelectric nonvolatile semiconductor memories (FeRAMs),non-volatile random access memory, sensor, microwave detectors etc. among them Bi-layered pseudo-perovskite a series of Bi-layered perovskite $ABi_2B_2O_9$has attracted much attention due to its excellent fatigue free characteristics in combination with low leakage current density, good hysteresis behavior, long data retention time and fast switching voltage behavior. Ferroelectricity having a series of Bi-layered perovskite $ABi_2B_2O_9$ was first discovered by Smolenskii. (1961). The general chemical formula of Bi-layered perovskite is as $[Bi_2O_2]^{2+}$ $[A_{m-1}B_mO_3{}^{m+1}]^{2-}$. A = Na^+, K^+,$Ba^{2+,}$ Ca^{2+}, Pb^{2+}, Sr^{2+}, Bi^{3+}, : B = Fe^{3+}, Ti^{4+}, Nb^{5+},Ta^{5+}, W6+, and m = 1 to 6]. $SrBi_2Ta_2O_9$is a well-known layered perovskite oxide, where perovskite-type groups$[SrTa_2O_7]^{2-}$ and semiconducting layers $[Bi_2O_2]^{2+}$are stacked alternately along the pseudo-tetragonal c-axis. The crystal structure of SBT is orthorhombic at room temperature with space group A21am (a = 5.531, b = 5.534, c = 25.984 A).

In this paper it is found that spontaneous polarization (Ps) of $SrBi_2Ta_2O_9$ is 5.8 $\mu C/cm^2$ along the a-axis at room temperature, while Ps = 26 $\mu C/cm^2$ in representative perovskite ferroelectric of $BaTiO_3$ along the tetragonal c-axis. The dielectric constant (ϵ) and the specific heat (C_p) of this crystal show very weak. The peak value of the dielectric constant is only 300atTc, which is two orders smaller than that of BaTiO3 (14, 000). Although SBT has been a key material of ferroelectric memory in recent years, detailed fundamental mechanism of this ferroelectric phase transition has not been discussed yet. In SBT, the -O-Ta-O-Ta-O- chain is interrupted by the existence of semiconducting $[Bi_2O_2]^{2+}$ layers, while the strongly correlated -O-Ti-O-Ti-O- chain plays an important role in the appearance of ferroelectricity in Perovskite BaTiO3.Many studies were done for ceramics and thin films, but a few for single crystals. It should be necessary for deep understanding of the ferroelectricity to investigate the nature of single crystals.

In this paper, the temperature dependence of specific heat, lattice constant and soft mode of SBT single crystal studied. Strontium bismuth tantalate has orthorhombic crystal structure with space group A21am in ferroelectric phase followed by tetragonal structure at/above 330 ^{o}C with space group I4/mmm inparaelectric phase.
The incorporation of any cations at any of the Sr, Bi-sites or Ta-sites will modify the crystal structure and symmetry depending on their valance and ionic radii of cations. Vibrational studies have been used to give the information about the displacements of the atoms or ions, some of which are related to the polarization of the material and Raman scattering is a useful tool for exploring the microscopic origin of the ferroelectricity of materials. Here none of the observations could assign all
the observed Raman and infrared modes also no theoretical calculation of phonons has been made in SBT in its orthorhombic (A21am) crystal structure. Here it is investigate the Raman and infrared phonons of SBT using normal coordinate analysis involving nine stretching and eight bending force constants. The theoretically obtained values are in very good agreement with the experimental ones. Here an effort is also made to assign experimental frequencies to their respective optical phonon modes. The potential energy distribution has also been investigated for determiningthe significance of contribution from each force constant towardthe Raman and infrared wavenumbers.

Chapter 2

2.0 Experimental Technique:-

The material is synthesized in solid state reaction route and put for characterization.

2.1 Synthesis in Solid State Route:-

The parent $SrBi_2Ta_2O_9$ material is synthesized by solid state route by taking stoichiometric formula in atomic weight percentage method .The reaction is given by

$$SrCO_3 + Bi_2O_3 + Ta_2O_5 \rightarrow SrBi_2Ta_2O_9 + CO_2$$

In case of doping with dysprosium the equation is modified as

$$SrBi_2Ta_2O_9 + Dy_2O_3 \rightarrow SrBi_{2-x}Dy_xTa_2O_9$$

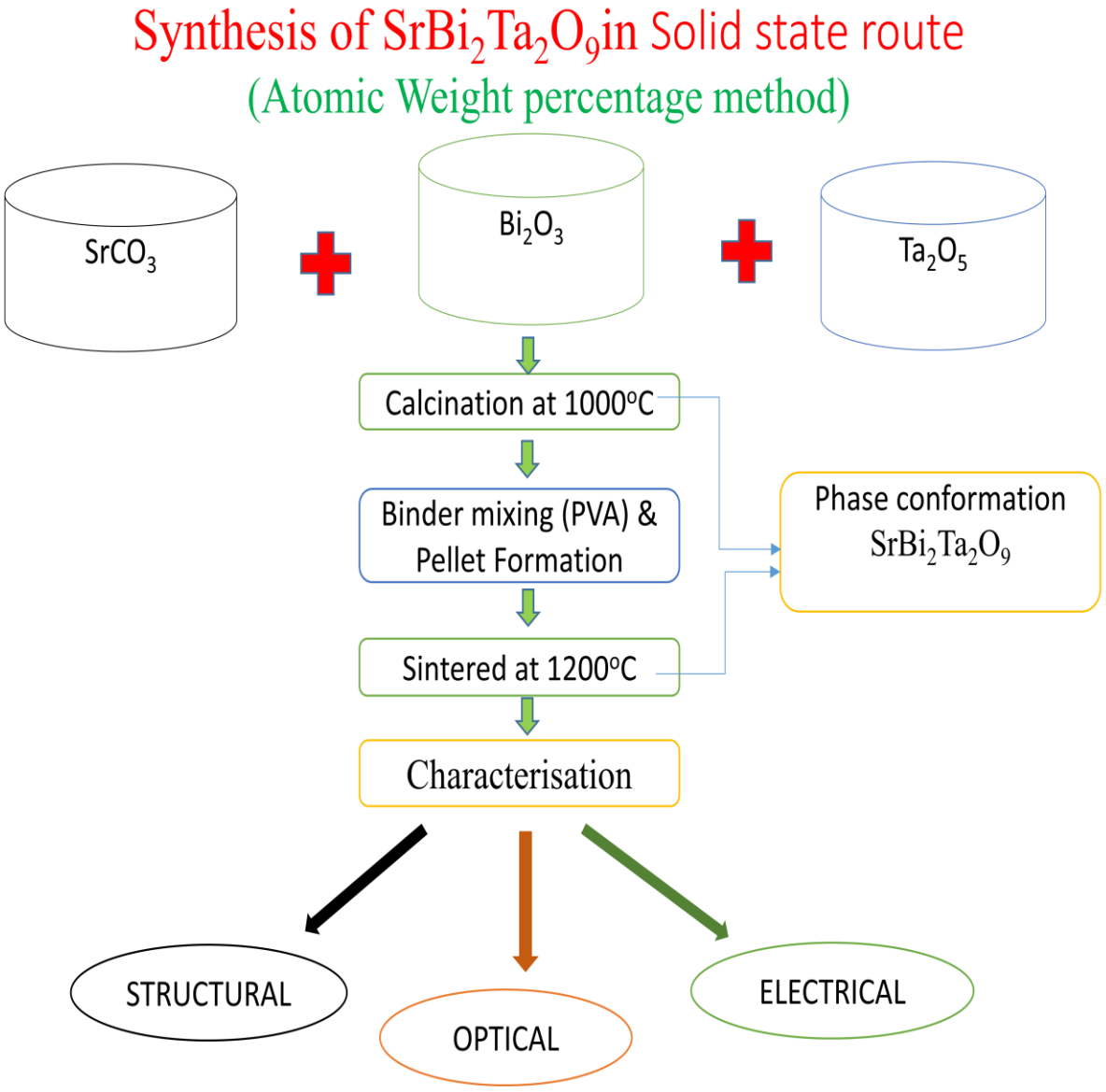

Fig: 5- Flow chart of SBT synthesis

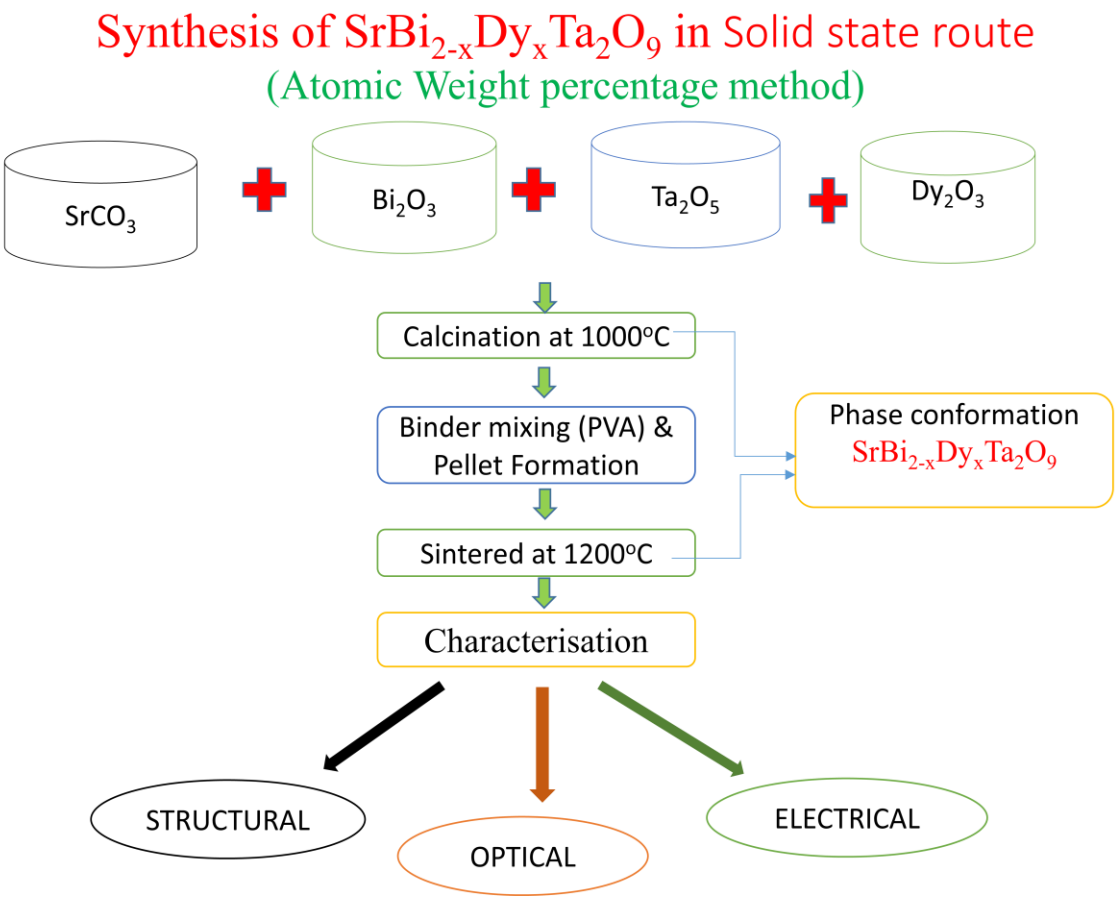

Fig.6 Flowchart of SBTDy Synthesis

2.2 Characterization technique:-

For structural properties XRD and SEM were done. For electrical properties P-E loop and dielectric measurement were done. For optical properties UV-VIS spectroscopy is done.

2.2.1 X Ray Diffraction Study:-

In atoms, Crystals are regularly arranged in different planes. The inter atomic distance between the atoms are in the order of ^{0}A. X-rays are electromagnetic radiation having wave length in the range of 1^0A-100^0A.the atomic planes distance and X-ray wave length are in the same range ,so atoms diffracts X-ray waves but the electrons scatter Xrays.

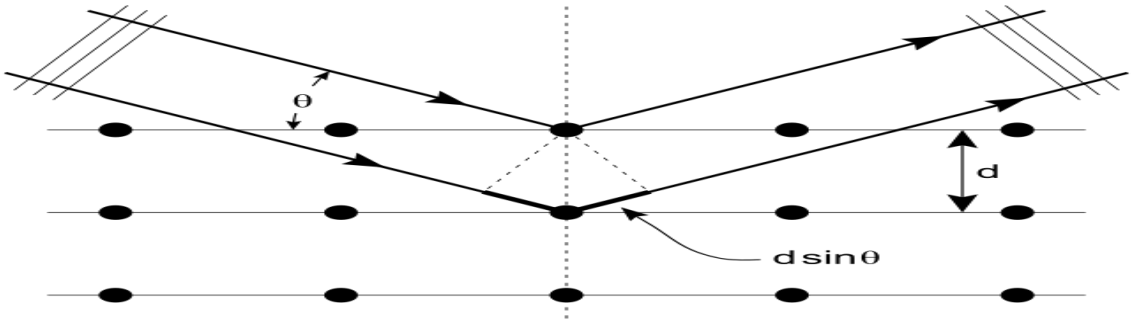

Fig7:-Diffraction of X-rays by Atomic Planes

According to Bragg's law: a regular array of atoms gives diffraction pattern when exposed to a suitable ration EM waves. Constructive or destructive diffraction pattern are observed in a few specific directions, determined by equation

$$2d\sin\theta = n\lambda$$

Here *d* = spacing between diffracting planes

θ= incident angle

n = integer, and

λ = wavelength of the beam.

2.2.2 SEM Study:-

SEM is used for the topographical and morphological study of specimen surface. In SEM, electron beam are generated by thermonically and by applying potential difference to an electron gun which is fitted with a tungsten filament known as cathode. Tungsten is used as electron guns because it possesses highest melting point and lowest vapor pressure among all metals, The electron beam has an energy ranging from 0.2 keV to 40 keV, is focused by one or two condenser lenses to a spot about 0.4 nm to 5 nm in diameter, then it passes through pairs of scanning coils and fall to the sample surface. The scatter and secondary electrons from the specimens are collected by the detectors then analyzed by computers and final image is generated.

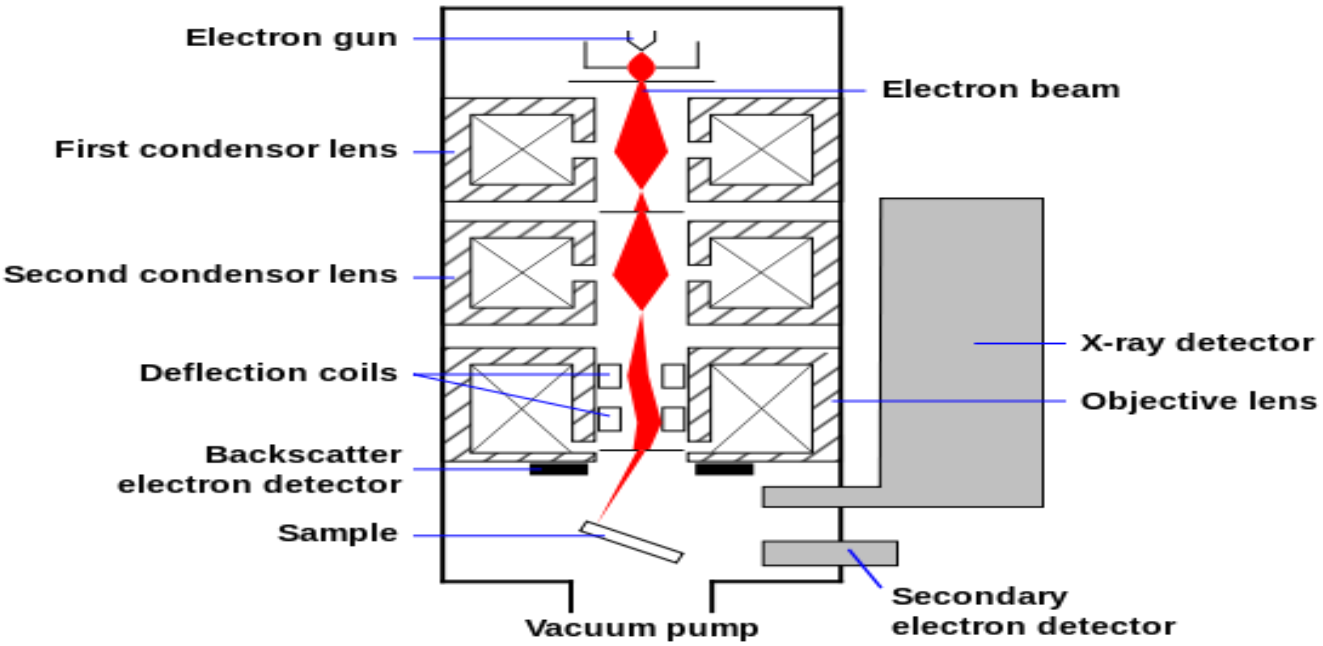

Fig:-8 Mechanism of scanning electron microscopy

2.2.3 Di-electric study:-

Dielectric constant is measure by using LCR setup .the

$C = \text{Ɛ}A/d = \text{Ɛ}_0\text{Ɛ}_r\ A/d$

$\text{Ɛ}_r = C * d/(\text{Ɛ}_0 * A)$

$$\mathbf{P} = \varepsilon_0 \chi_e \mathbf{E},$$

Where ε_0 is the electric permittivity of free space.

The susceptibility of a medium is related to its relative permittivity ε_r by

$$\chi_e = \varepsilon_r - 1.$$

So in the case of a vacuum,

$$\chi_e = 0.$$

The electric displacement **D** is related to the polarization density **P** by

$$\mathbf{D} = \varepsilon_0 \mathbf{E} + \mathbf{P} = \varepsilon_0 (1 + \chi_e) \mathbf{E} = \varepsilon_r \varepsilon_0 \mathbf{E}.$$

In general, a material cannot polarize instantaneously in response to an applied field. The more general formulation as a function of time is

$$\mathbf{P}(t) = \varepsilon_0 \int_{-\infty}^{t} \chi_e(t - t')\mathbf{E}(t')\, dt'.$$

2.2.4 Hysteresis Study:-

Hysteresis occurs in ferroelectric material in the response of varying force generated by applied electric field. The ferroelectric material retain some polarization even in the absence of external field known as remanent polarization.at higher field the polarization value saturates and it is known as saturation polarization.to make the polarization value zero negative field is (Ec)required and this field is called cohesive field.

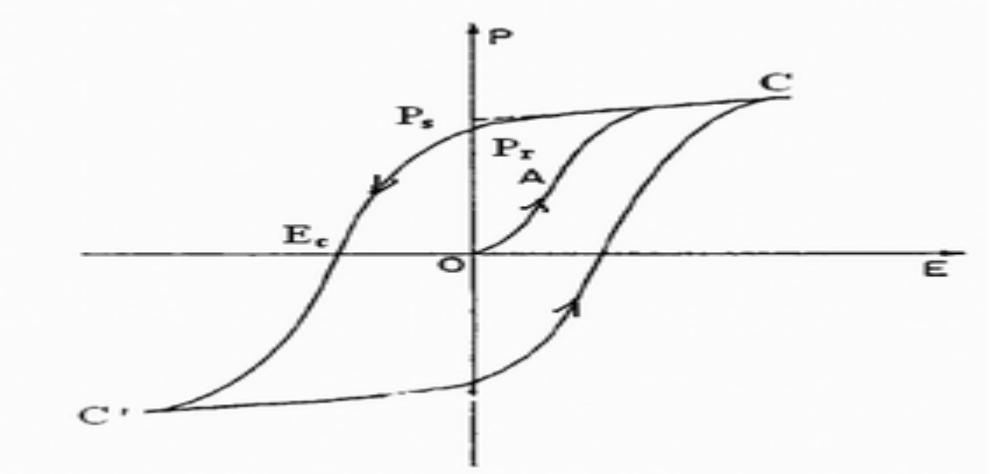

Fig9: Hysteresis behavior of ferroelectric material.

2.2.5 UV-VIS Spectroscopy:-

Ultraviolet–visible spectroscopy refers to absorption spectroscopy or reflectance spectroscopy in the ultraviolet-visible spectral region. Where light in the visible and

adjacent near-UV and near-infrared (NIR) ranges. The absorption or reflectance in the visible range directly affects the perceived color of the chemicals involved to the sample. In UV-VIS electromagnetic spectrum, molecules undergo electronic transitions. This is a complementary technique fluorescence spectroscopy where fluorescence deals with transitions from the excited state to the ground state, while absorption measures transitions from the ground state to the excited state.

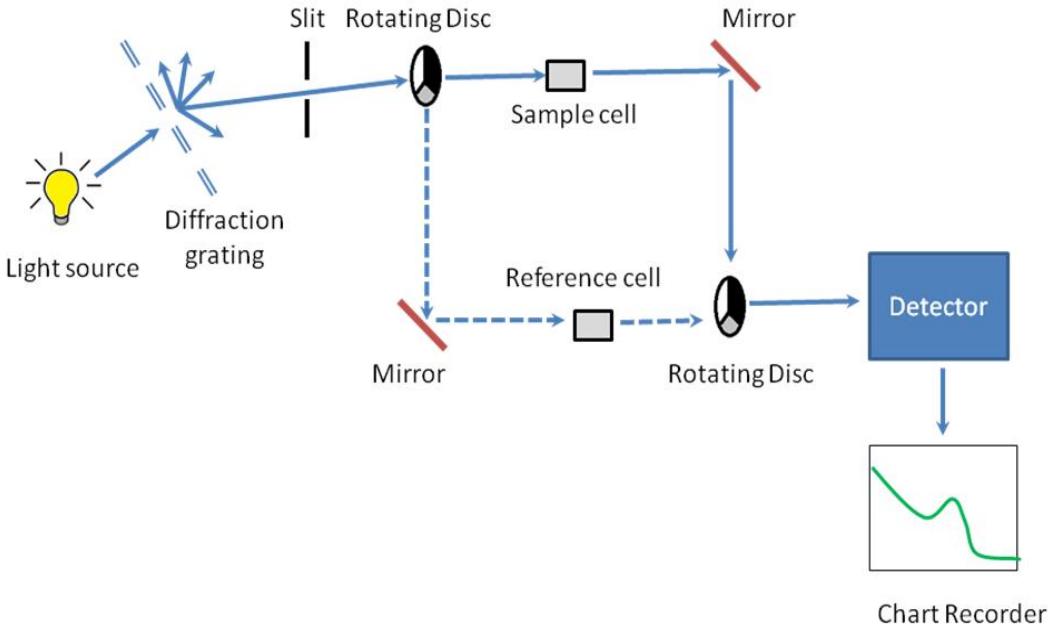

Fig10:-UV-VIS Spectroscopy

Molecules containing π-electrons or non-bonding electrons (n-electrons) can absorb the energy in the form of ultraviolet or visible light to excite these electrons to higher anti-bonding molecular orbitals. The more easily excited the electrons (i.e. lower energy gap between the HOMO and the LUMO), the longer the wavelength of light it can absorb.

Using the Beer-Lambert law: absorption is calculated

$$A = \log_{10}(I_0/I) = \epsilon \cdot c \cdot L,$$

Where A = absorbance,

I_0= intensity of the incident light at a given wavelength,

I = transmitted intensity,

L = path length through the sample,

c = concentration of the absorbing species,

ε = extinction coefficient

Chapter 3

Result and Discussion

3.1 XRD Analysis:-

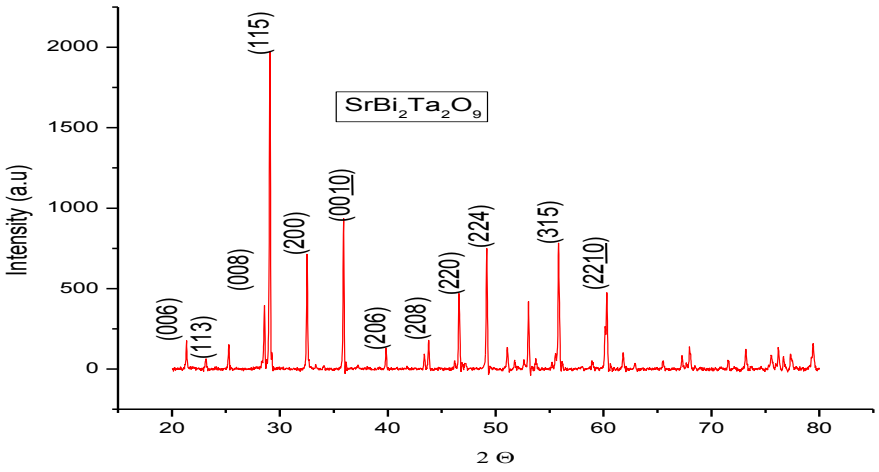

Fig11:- XRD of $SrBi_2Ta_2O_9$

Fig.11 shows the XRD (JCPDS-81-0552) it was confirms the presence of $SrBi_2Ta_2O_9$, the desired composite. The main peaks appears at (115) planes and in both sides peaks are no uniformly. Some extra peaks were observed which indicates the presence of impurities in the prepared sample.

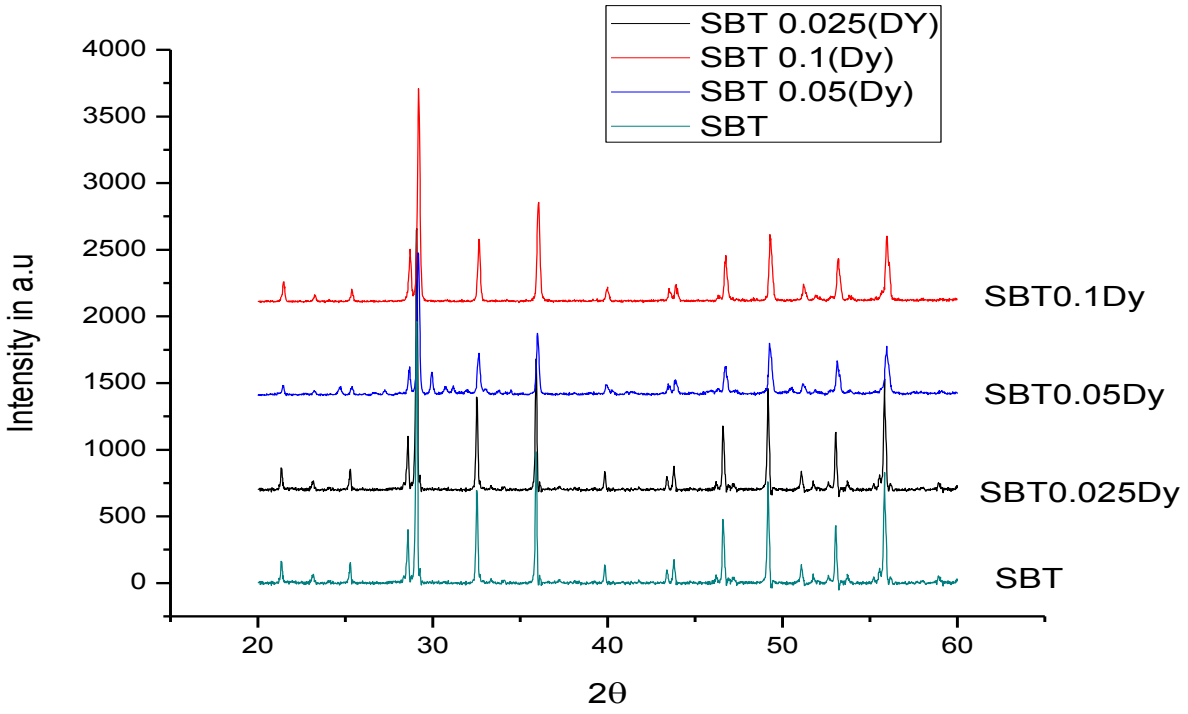

Fig12:- XRD of $SrBi_{2-x}Dy_xTa_2O_9$,(x=0.025,0.05,0.1)

Fig.12 shows the XRD pattern of $SrBi_{2-x}Dy_xTa_2O_9$ ceramic different with value of x(0.025,0.05,0.1) and the samples are sintered at 1200^0C . The XRD patterns of the sample are well consistent with the JCPDS 81-0552[$SrBi_2Ta_2O_9$].The SBTDy ceramics shows secondary phase formation of Dy-oxide, which indicates all the Dy doped SBT samples are pure in phase of bismuth layered structure with m=2.The crystal symmetry of the sample is orthorhombic with the shifting of the highest intensity peak toward the higher diffraction angle, because of the lower side of the Dy^{3+} with respect to the Bi^{3+}.

3.2 SEM Analysis:-

Fig.13 shows the SEM of parent and doped sample, the parent material $SrBi_2Ta_2O_9$ have irregular type of grain size. When Dy3+ is doped the grain are continuously towards homogeneity.

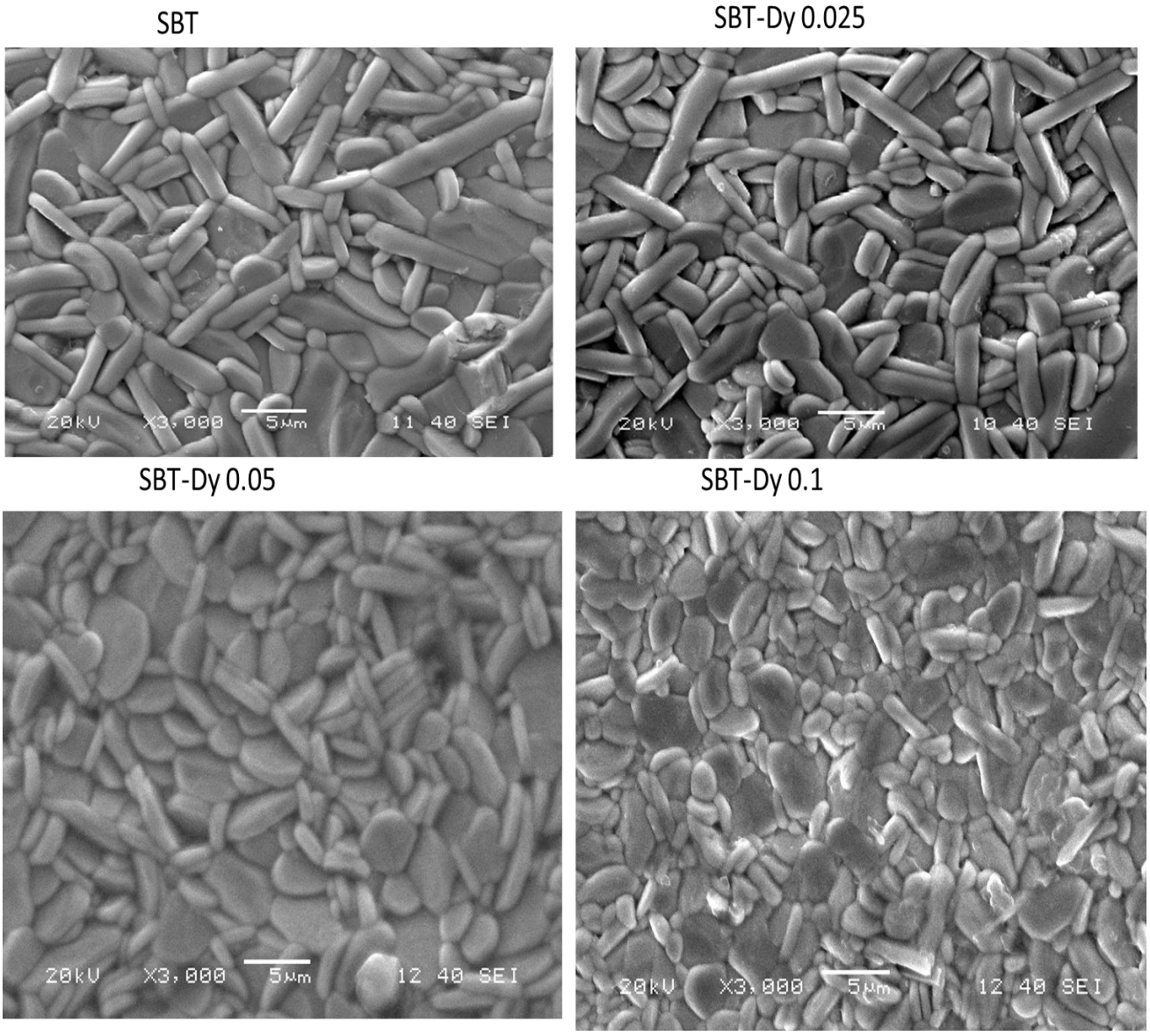

Fig13:-SEM Image of SBT and SBTDy

3.3 Dielectric analysis:-

From the dielectric constant data, T vs. Ɛr increases with increasing of temperature having two peaks, one at lower temperature and another at high temperature which is called transition temperature(Tc).At Tc the structure change from Orthorhombic to Tetragonal.it is also confirms that Tc increases with increasing doping concentration.

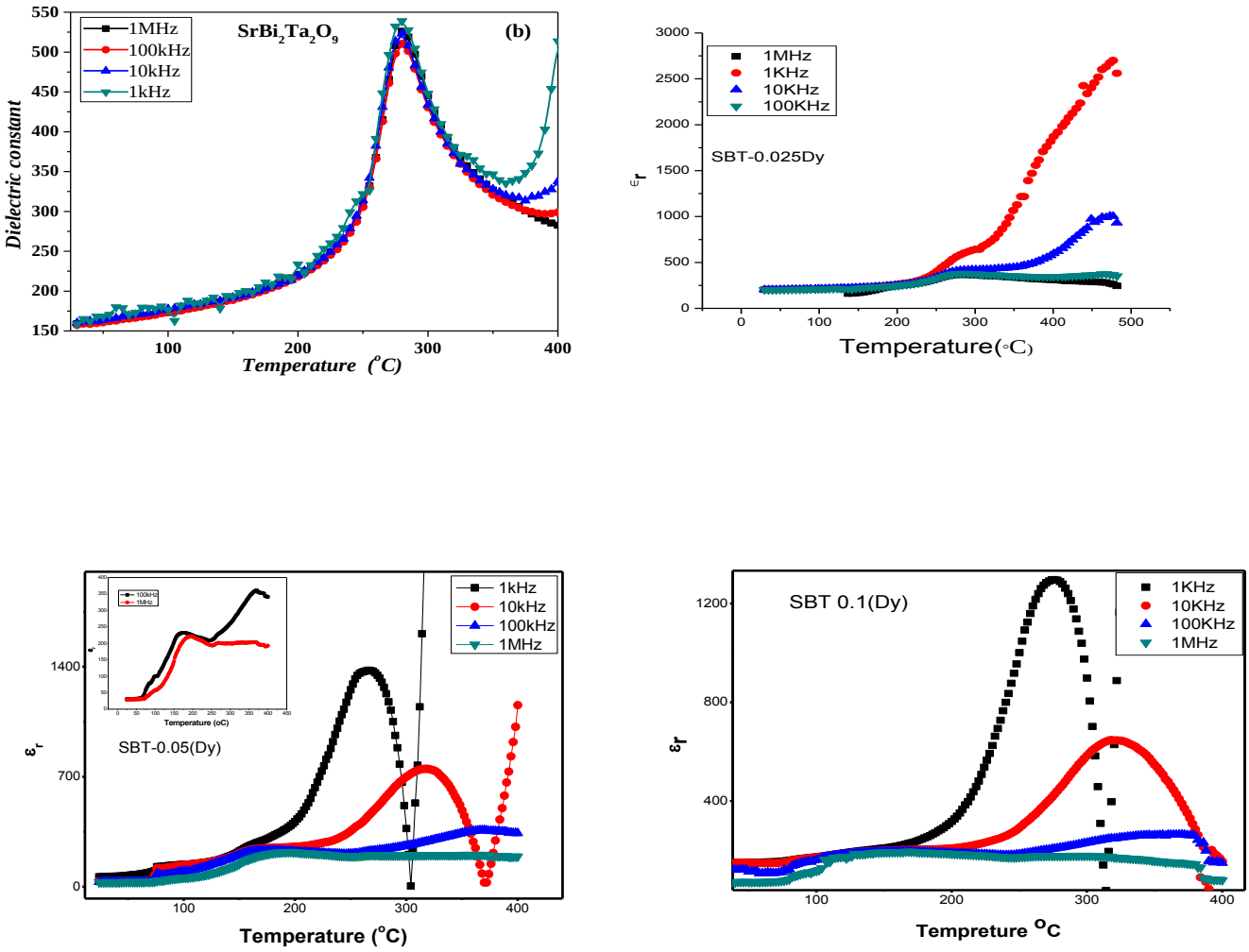

Fig.14 Dielectric constant comparison of SBT to SBTDy

Fig.15 shows the tangent loss of parent to doped sample. The dissipation factor or tangent loss gradually increasing with temperature for parent and also for doped sample.

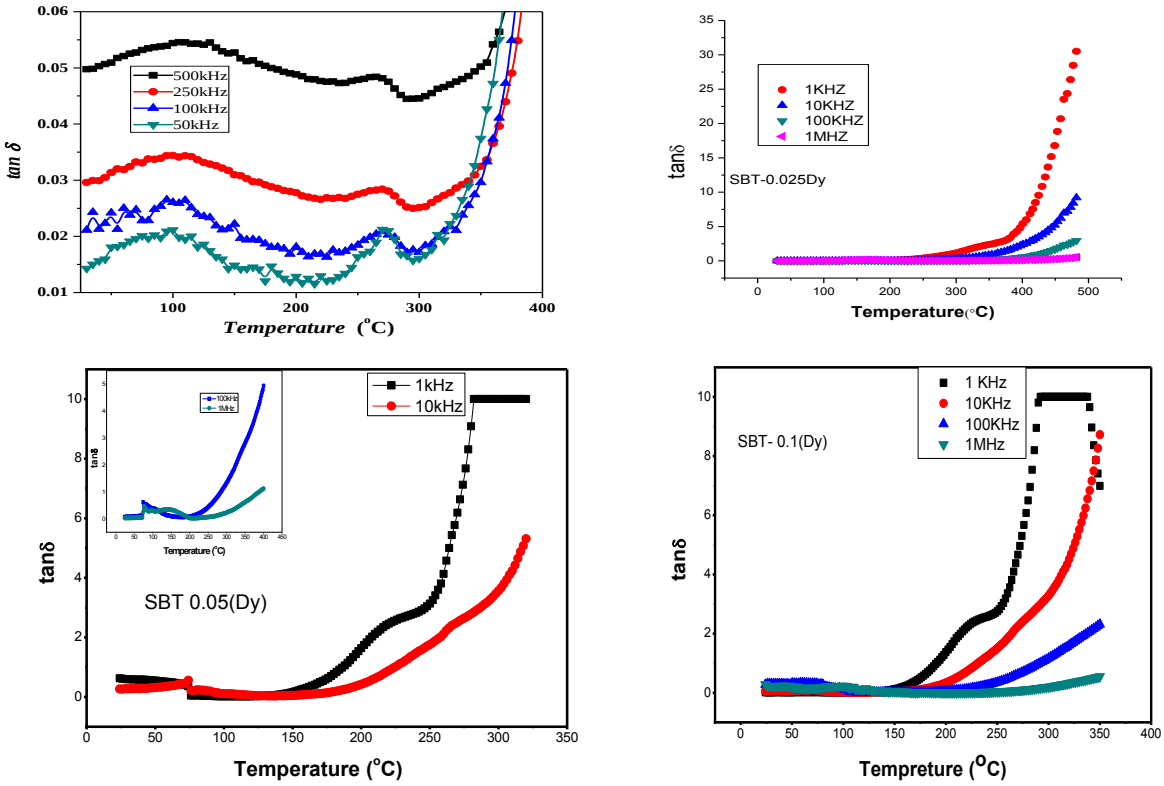

Fig. 15 Tangent loss of SBT and SBTDy

3.4 P-E Loop Analysis:-

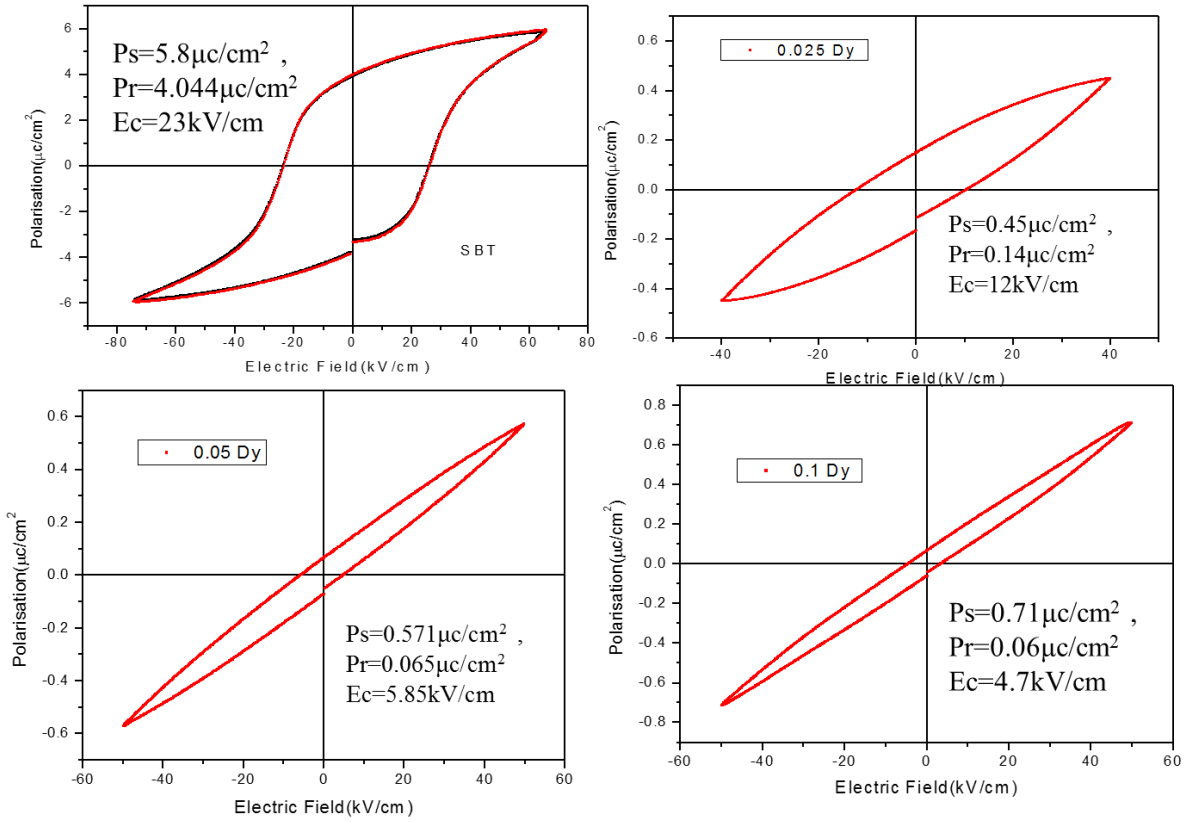

Fig.16 P-E Loop analysis of SBT and SBTDy

From Polarization (P) vs Electric field (E) is is confirm that for parent material have well saturation polarization having remanent polarization Pr=4.044 µc/cm^{2}and saturation polarization Ps=5.8µc/cm^2. When Dy^{3+} content increases both Pr and Ps value gradually decreases.

	Parent SBT	SBT-0.025Dy	SBT-0.05Dy	SBT-0.1Dy
Ps (µc/cm^2)	5.8	0.045	0.57	0.071
Pr (µc/cm^2)	4.044	0.14	0.065	0.06
Ec (kV/cm)	23	12	5.85	4.7

3.5 UV-VIS Analysis:-

From UV-VIS result it is confirmed that as Dy^{3+} doped content increases the band gap of the sample gradually decreases. Hence doping concentration increases the semiconducting properties.

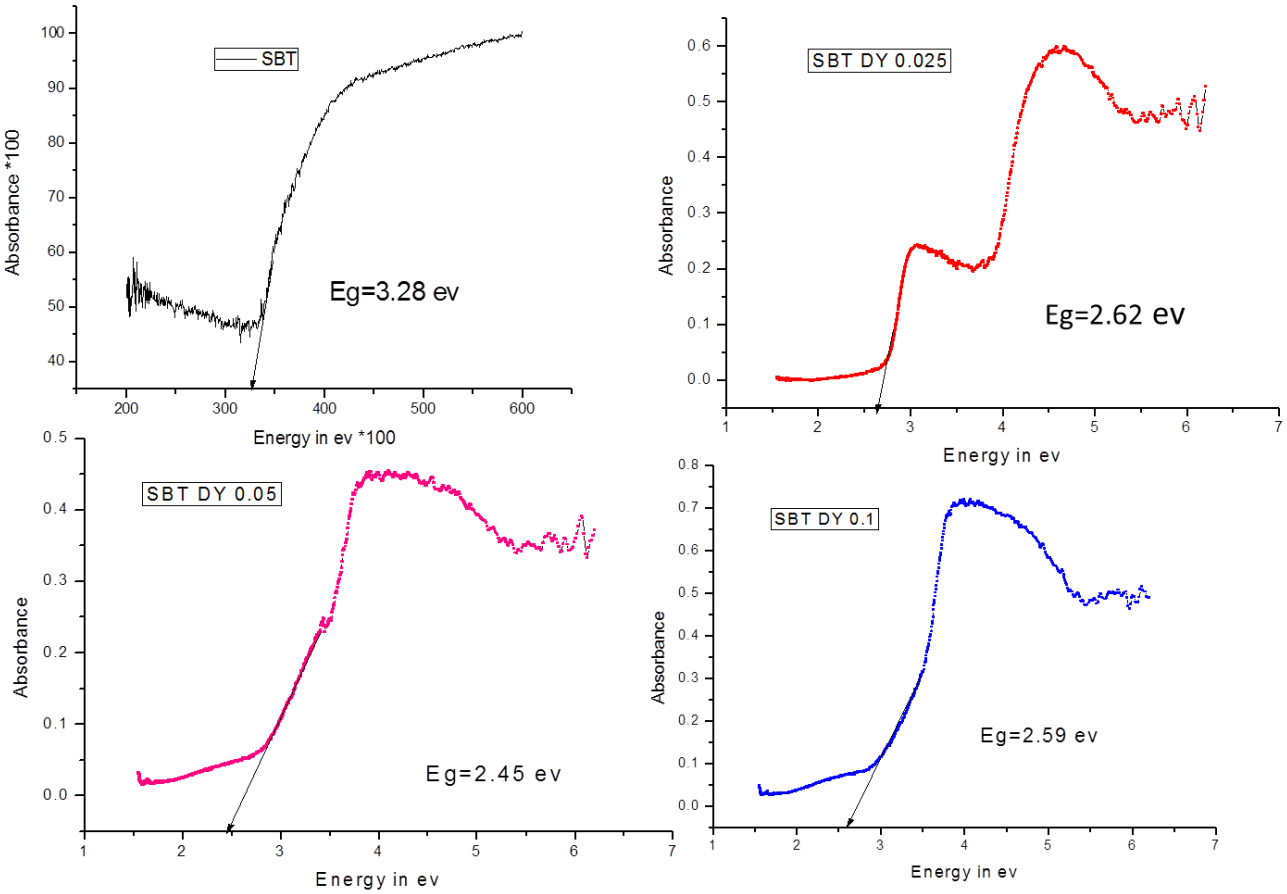

Fig.17 UV-VIS Analysis of SBT and SBTDy

Chapter 4

4.1 Conclusion:-

Dy doped does not change the structure of SBT but the lattice parameters decreases as the peaks are shifted towards the higher diffraction angle. From structure morphology study it's confirm that the grains are increasing uniformly with increasing of Dy^{3+} content. Dielectric constant and tangent loss increases with increase of temperature. The doping concentration increases the semiconducting behavior of the parent material which is confirmed from the UV-VIS result.

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